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Great Lakes National
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EPA

Report On An Investigation Of Sediment Contamination

The Milwaukee Estuary Wisconsin

Sampled July 29-31, 1980

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For

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Table of Contents

FOREWORD

The Great Lakes National Program Office (GLNPO) of the United States Environmental Protection Agency was established in Region V, Chicago, to focus attention on the significant and complex natural resource represented by the Great Lakes.

GLNPO implements a multi-media environmental management program drawing on a wide range of expertise represented by universities, private firms, State, Federal, and Canadian governmental agencies, and the International Joint Commission. The goal of the GLNPO program is to develop programs, practices and technology necessary for a better understanding of the Great Lakes Basin ecosystem and to eliminate or reduce to the maximum extent practicable the discharge of pollutants into the Great Lakes system. GLNPO also coordinates U.S. actions in fulfillment of the Great Lakes Water Quality Agreement of 1978 between Canada and the United States of America.

TABLES

FIGURES

I. SUMMARY

The sediment samples collected in the Milwaukee Estuary on July 29-31, 1980 show low to moderate levels of organic contaminants and moderate to high levels of inorganic contaminants. The results show similar levels of polychlorinated biphenyls (PCB) contamination as was found in previous surveys of the same areas. Although increases in PCB levels with depth in the sediment column were found at some sites, no pockets of severe PCB contamination were found in the 1980 study area.

Polynuclear aromatic hydrocarbons were found to be at low to moderate levels in this survey.

The quality control, sample analysis procedures, and analytical results for the data were reviewed for reasonableness and consistency. The data was judged to be acceptable on the basis of the review.

II. CONCLUSIONS

1. Sediments in the Milwaukee Estuary contain high concentrations of conventional inorganic pollutants and heavy metals, and detectable levels of a number of organic priority pollutants.

2. Contaminant levels are generally highest in the upper sediment layers, indicating probable recent input of pollutants to the Estuary.

3. Major source areas of pollutants appear to be; upstream of 25th Street on the Menomonee River, the Menomonee Canal, the Jones Island STP, and on the Kinnickinnic River between Kinnickinnic Avenue and the Kinnickinnic Basin.

4. There are few direct industrial process discharges into the Milwaukee Estuary. Most such discharges are directed to the Jones Island Municipal Sewage Treatment Plant (STP) by sanitary sewers. During rainfall events, it is possible that process wastes mixed with storm water are discharged directly to the Estuary through combined sewer overflow (CSO).

5. Contaminants that are apparently due primarily to combined sewer overflow discharges include phosphorus throughout the Estuary, polynuclear aromatic hydrocarbons (PNAs) on the Milwaukee River between Walnut Street and St. Paul Avenue, and polychlorinated biphenyls (PCBs) on the Kinnickinnic River.

6. Sediment PCB levels have remained constant since the mid 1970's. Although sediment PCB levels did increase with depth in the sediment column at some sites, there were no pockets of severe contamination found in the 1980 study areas. However, based upon sampling by others, PCB concentrations are likely to exceed 50 mg/kg in portions of the outer harbor.

7. The nature and degree of sediment contamination in the Estuary is comparable to major industrialized Great Lakes harbors subject to large numbers of direct industrial discharges.

III. SEDIMENT SURVEY OF JULY 29-31, 1980

Previous sediment surveys in the Milwaukee Estuary showed significant sediment contamination with a wide range of pollutants. However, the studies were limited in scope and in pollutants measured, and/or were surface grab samples only. Contaminant concentrations in sediments can be highly variable with depth. The deeper (older) sediments are often more contaminated as of results of historical, less stringently regulated discharges than are the surface (recent) discharges. In order to better define the nature (kinds of pollutants) and extent (variation with depth and along the rivers) of sediment contamination in the Milwaukee Estuary, the USEPA Great Lakes National Program Office (GLNPO) contracted with the University of Wisconsin Milwaukee, Center for Great Lakes Studies (CGLS) to collect sediment core samples at 23 representative locations (Figure 1 and Table 1) within the Estuary. The samples were collected in the period, July 29-31, 1980.

The samples were analyzed by Envirodyne Engineers, St. Louis, Missouri under contract to the USEPA Central Regional Laboratory (CRL), Region V.

A. SAMPLING METHODS

Sediment core samples were obtained utilizing the CGLS RV Neeskay on July 30 and 31, 1980. On July 29, 1980, a Boston Whaler was used upstream of St. Paul Avenue (sample sites 14-16) on the Milwaukee River and upstream of Rogers Street on the Kinnickinnic River (sampling site 10) to allow passage under stationary bridges too low for the Neeskay to pass under. Only surface grab samples were collected from the Boston Whaler due to the weight and unwieldiness of the core sampler.

Grab samples were collected with a Wildco No. 1725 G10 sampler. Core samples were collected with a Benthos No. 2171 gravity corer equipped with a stainless steel nosecone, core catcher, and liner (2-1/2" I.D.), all of which were rinsed with analytical grade n-hexane prior to sampling. The core samples were extruded in 30 cm (approximately 1 ft.) lengths into glass containers that had been previously rinsed with hexane. Aluminum foil was placed over the container mouths prior to closure. The samples were stored in a refrigeration unit at or near 4°C prior to transport to the CRL in Chicago. The samples were transferred to well-insulated blood storage boxes with ice for the two hour drive to Chicago.

Pertinent sample information and general observations were recorded in a boring log. 35mm color slides were taken of the vicinity of each sampling site to aid in sampling site documentation. EPA chain-of-custody procedures were employed (NPDES Compliance Sampling Inspection Manual MCD-51, USEPA).

For sampling quality control purposes, replicate cores were taken in close proximity at sites 7 and 11.

Samples from sites 14, 16, 20, and the 60-90 cm section from the site 19 sample were lost in a handling accident at the CRL while they were being prepared for shipment to the contractor for analysis. There are, therefore, no chemical analyses available for those samples.

TABLE 1

Sample Sites - Milwaukee Estuary, July 29-31, 1980

Sample Site Number	Description
1	Outer Harbor
2	Near Jones Island Sewage Treatment Plant Outfall
3	Inner Harbor Entrance Channel at Daniel Webster Hoan Bridge
4	Milwaukee River and Kinnickinnic River Confluence
5	Kinnickinnic River at Greenfield Avenue
6	Central Kinnickinnic Basin
7	North East End of Kinnickinnic Basin
8	Kinnickinnic River at Kinnickinnic Avenue
9	Kinnickinnic River at Rogers Street
10	Kinnickinnic River at Lincoln Avenue
11	Milwaukee River at Florida Street
12	Milwaukee River at Menomonee River Confluence
13	Milwaukee River at St. Paul Avenue
14	Milwaukee River at Highland Avenue
15	Milwaukee River at Walnut Street
16	Milwaukee River at Humboldt Boulevard
17	Confluence of Menomonee River and Menomonee Canal
18	Confluence of Menomonee Canal and Burnham Canal
19	Menomonee Canal at 11^{th} Street
20	Burnham Canal at 10^{th} Street
21	Menomonee River at 7^{th} Street
22	Menomonee River at Muskego Avenue
23	Menomonee River at 25^{th} Street

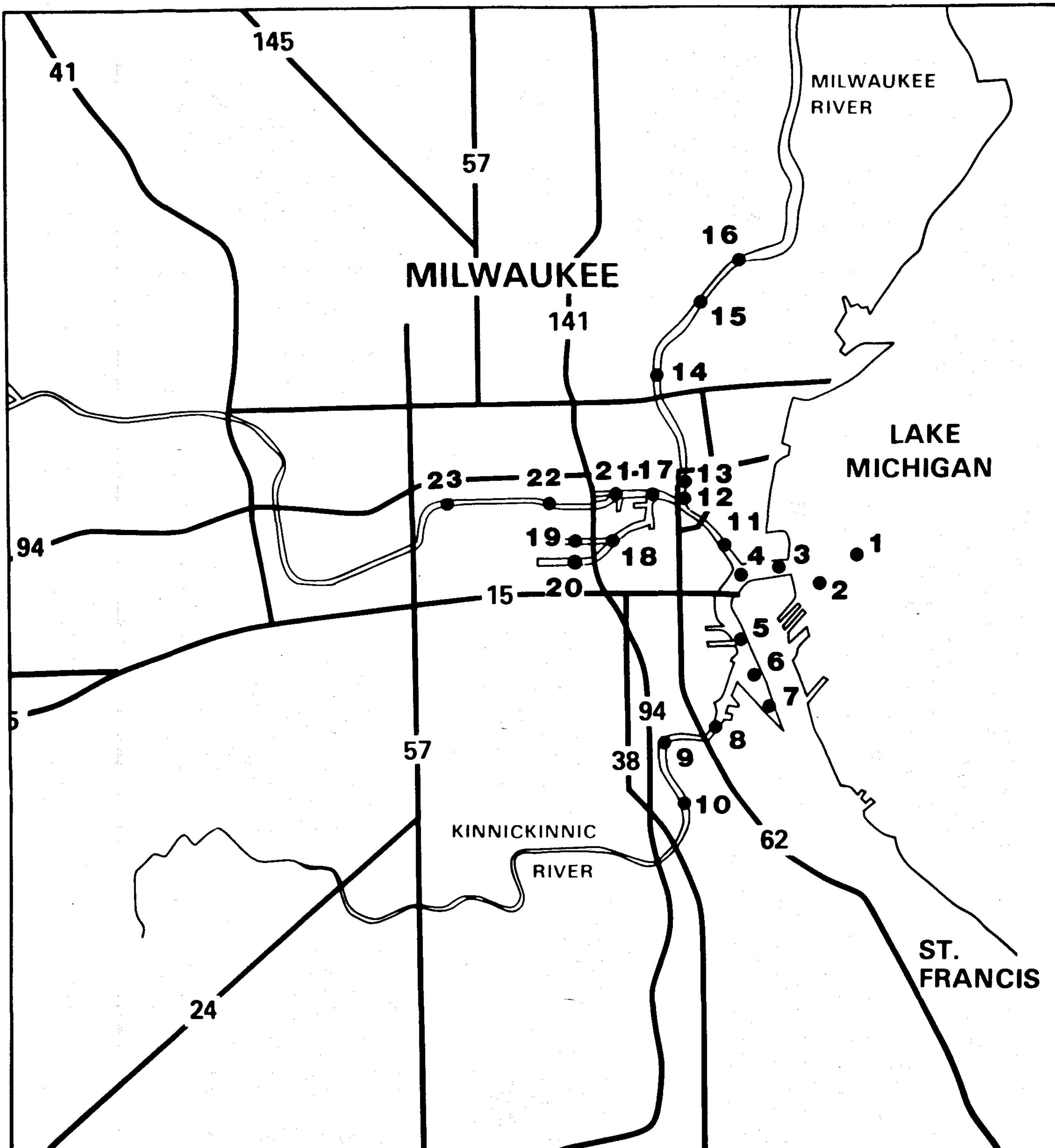

Figure 1. Sediment Sampling Sites
July 29-31, 1980

B. ANALYTICAL METHODOLOGY AND PROBLEMS ENCOUNTERED

The analytical methods employed for this study are outlined in Table 2.

This section contains a discussion of the problems encountered in employing each of the analytical methods.

Chemical Oxygen Demand (COD)

The only difficulty that was encountered during this analysis was the observance of high concentrations in most of the samples. This problem was overcome by using only 0.2g of sample for the analysis which put most of the samples within the analytical range.

Total Phosphorus

Problems were encountered with color stability using the 2-reagent ascorbic acid method. Although this method claims that the color should be stable after five minutes and good for one hour, the analyst found that the color kept deepening beyond the five minute period. To overcome this problem, the analyst switched to a stannous chloride method and used 5 ml of H_2SO_4 as suggested by the USEPA task officer.

The ascorbic acid method had been used during the analysis of the first 10 percent of the samples. Since these results appeared to be higher than expected due to the instability of the color using this method, the samples were rerun using the stannous chloride method. The earlier results were discarded.

The perchloric acid digestion was not used during the analysis due to the lack of a hood for safe performance of this procedure. The modification had been cleared with the USEPA task officer during his site visit. Further, 5 ml rather than the 1 ml of sulfuric acid suggested in the agreed-upon method was employed. This modification was found to give a better recovery on the NBS standard sediment.

Ammonia

Problems were encountered with precipitate formation and low recoveries during analysis of the first 10 percent of the samples. The laboratory at that time switched to the automatic method referenced in Table 2. Because of the better quality control (QC) results obtained with this method, the first 10 percent of the samples were reanalyzed using the latter method and earlier results discarded.

TABLE 2

ANALYTICAL METHODOLOGY

TKN	CLM*	Page 43
Ammonia	CLM*	Page 36
Total Solids	CLM*	Page 3
Volatile Solids	CLM*	Page 5
COD	Chemistry Laboratory Manual for Bottom Sediments, Great Lakes Region December 1969	Page 5
Phosphorus	Standard Methods, 14th Edition Method 425E	Page 479
Cyanide	CLM*	Page 25 except manual colorimetric measurement
Phenol	CLM*	Page 90
Oil & Grease	CLM*	Page 103
Metals	CLM*	Page 69
Mercury	Methods for Chemical Analysis of Water and Waste, EPA, March 1979 No. 245.5	Page 69
Pesticides/PCB's	Extraction by CLM* Followed by Cleanup using EPA Method #608, Federal Register, December 3, 1979	Page 108
Acid, Base/Neutral, Organic Priority Pollutants	CLM*	Page 140

*CLM - Chemistry Laboratory Manual for Bottom Sediments and Elutriate Testing, EPA-905/4-79-014, USEPA, Region V, March 1979

Total Kjeldahl Nitrogen (TKN)

The methodology employed for this analysis was also changed from a manual to the automated method listed in Table 2. This was found to produce much better results on the NBS standard sediment sample as well as results in the range anticipated by EPA. For this reason, the first 10 percent of the samples were rerun using the automatic method and the earlier results discarded.

Phenols

High spike recoveries were encountered during this analysis. This may be due to a slight variation in the logistics of running the samples versus the spikes. Samples were manually distilled and the distillates held until a complete set was available to be put on the Technicon. However, the spikes were distilled and run immediately. The high spike recoveries may, therefore, be due to loss of phenols in the distillates during storage.

Cyanide

In reviewing the data for the first 10 percent of the samples, it was noted that these were calculated incorrectly. The correct data are reported in this report.

Metals

Standard additions were found to be necessary on all samples in the first batch of samples analyzed. Because of matrix variations, however, standard additions were found to be necessary in only 30-40 percent of the remaining samples in which high organic interferences were encountered.

Spike recoveries on some of the samples fall slightly outside of the perscribed range. This is probably due to the inaccuracy introduced by dilution of the samples and spikes in order to put them within the analytical range. Dilution was found to be necessary on almost all samples being analyzed for selenium, arsenic, manganese, cobalt and zinc.

Mercury analyses were all performed in duplicate, the reported value being the average of the two determinations.

Pesticides/PCB's

High sulfur interferences were encountered in most samples, requiring that most samples be treated two to three times with mercury or copper to eliminate the interferences. In addition, most samples had to be run at more than one dilution even after florisil cleanup due to high background levels. Pesticide analyses were not confirmed by GC/MS.

Gas Chromatography/Mass Spectrometry (GC/MS)

Almost all of the samples analyzed were found to be extremely dirty, creating problems with both their preparation and the analysis. Emulsions were encountered in almost all cases during the base/neutral acid-washing separation procedure. Concentrations were found to take additional time and several samples could not be reduced to the level specified in the method because of the high organic content.

Instrumental problems were a result of the high hydrocarbon backgrounds encountered which made it difficult to identify and quantify the priority pollutants as well as to perform the library searches. Although the Quantid program was employed for the priority pollutants, it was found to not always be capable of picking out the peaks of these compounds. This was also probably due to the high backgounds encountered and mandated some manual data reduction to assure the accuracy of the analysis.

C. RESULTS AND DISCUSSION

FIELD OBSERVATIONS

Field observations made on the sediment samples as they were collected were recorded in a boring log (Appendix A, Table A). Sediments in the Milwaukee River upstream of St. Paul Avenue were described as mud or muddy sand with organic detritus, having an earthy odor. Sediments in the vicinity of St. Paul Avenue had an oily odor. Sediments at the junction of the Milwaukee River and Menomonee River were grey clay indicating a scoured (non-depositional) area. Sediments in the Menomonee River, Menomonee Canal, and the Burnham Canal were described as black mud over grey clay having a hydrocarbon and/or disagreeable odor. Sediments in the Kinnickinnic River upstream of Kinnickinnic Avenue were described as mud with an earthy odor, while sediments further downstream were characterized as having an oily/hydrocarbon odor. Sediments in the Milwaukee River downstream of the Menomonee and Kinnickinnic River junctions, in the Inner Harbor Entrance Channel were described as dark gray to black mud with an earthy odor. Hard grey clay was found at sample site 1 in the Outer Harbor indicating a scoured area. Sediments adjacent to the Jones Island Municipal Sewage Treatment Plant (STP) were found to have a stale odor.

Based upon the field observations, it appears that the major sources of petroleum contamination of the sediments are situated: along the Menomonee River beginning upstream of 25th Street; along the Menomonee Canal; along the Burnham Canal; on the Kinnickinnic River downstream of Rogers Street; and in the Kinnickinnic Basin vicinity. The degraded sediment conditions at St. Paul Avenue on the Milwaukee River are probably from an upstream source or sources on the Menomonee River (see following discussion under oil and grease).

POLLUTANT CONCENTRATIONS

Unlike the case of a deep lake depositional area, sediments in the estuary rivers are not likely to have been deposited in a vertically sequential manner (new sediments always covering the older sediments) due to disturbances from dredging and resuspension from navigation, CSO discharges, storm water flows, and flow augmentation of the Milwaukee River and Kinnickinnic River via flushing tunnels. The estuary has very complex hydraulics due to the interaction of the three rivers and Lake Michigan. Wisconsin Electric Power Company (WEPCO) withdraws cooling water (about 250 cfs) from the Menomonee River near South 10th Street (extended) and discharges heated water to the South Menomonee Canal. Since the average flow of the Menomonee River is only about 90 cfs, water is often drawn upstream along the bottom from Lake Michigan and the Milwaukee River (Harleman and Stolzenbach, 1967). Thus, the vertical sediment profile most likely does not accurately represent a time history of sediment deposition. Also, sedimentation rates within the estuary are likely to be highly variable between locations.

Therefore, rather than comparing pollutant concentrations from a particular strata (0-30 cm, 30-60 cm, etc.,) for all the sites sampled, it seemed more appropriate to compare the maximum concentrations at each sampling site. The following discussion of variations in pollutant concentrations within the estuary is based on this type of a comparison. Using this approach produced rather consistent patterns in pollutant variation within the estuary, whereas earlier investigations (Rexnord, 1979) generally reported similar concentrations throughout the estuary. It should be noted that these studies did find differences between the river sediments upstream of the estuary and those within the estuary, which was the primary purpose of those investigations. The apparent source areas for various pollutants based upon the patterns observed in the sediments are summarized in Table 3 and discussed below.

Sites 1 and 12 were scoured and generally had low pollutant concentrations. The discussion will, therefore, omit these sites unless something unusual was found. Overall contaminant levels are highest within the upper 60 cm of the core samples. Therefore, only exceptions to this will be noted in the discussion. It should be noted, however, that since compaction factors (i.e. depth of sediment penetrated vs length of sediment column retrieved in core barrel) were not determined, it is not known whether this 60 cm of sediment in the core tube represents 60 cm of in-place sediment or a much greater amount. Additionally, since no dating of the sediments was done and deposition rates are unknown, it is not possible to determine how recent the sediments in the top 60 cm are. However, the vertical variation observed indicates a probable recent input of pollutants to the estuary. Site 2 is located just off the Jones Island Sewerage Treatment Plant (STP) outfall. The STP is likely the source of much of the sediment contamination at that site. However, some of the contaminants may also be the result of sediments from the other estuary rivers settling out in the Outer Harbor, where there is a sudden decrease in velocity from that in the Inner Harbor Entrance Channel.

TABLE 3

Summary of Apparent Source Areas for Various Contaminants

Area	Contaminants
Milwaukee River	
Upstream of Walnut Street	Phenols
Upstream of St. Paul Avenue	PNAs
Jones Island STP	Oil and Grease, Phosphorus, Ammonia, TKN, Volatile Solids, COD, Phenols, Mêtals, Cyanide, Selenium, PCBs, PCP, Heptachlor, Phthalates, 2,4-dinitrotoluene
CSOs (throughout)	Phosphorus
CSOs (Walnut Street to St. Paul Avenue)	PNAs
Menomonee River	
Upstream of 25th Street	Oil and Grease, Ammonia, TKN, Volatile Solids, COD, Metals, Phthalates, PNAs
25th Street to Muskego Avenue	Phenols, Cobalt
Upstream of 7th Street	PCBs, Cyanide
Menomonee Canal	Oil and Grease, Ammonia, TKN, Volatile Solids, COD, Metals, Phthalates
Menomonee Canal/Burnham Canal Junction	Tin
Menomonee River/Menomonee Canal Junction	Tin
CSOs (throughout)	Phosphorus
Kinnickinnic River	
Upstream of Lincoln Avenue	Phenols
Upstream of Kinnickinnic Avenue	Oil and Grease, Volatile Solids, COD, Metals, Phthalates, PNAs
Kinnickinnic Basin	Oil and Grease, Ammonia, TKN, COD, Volatile Solids, Metals, Cyanide, PNAs, Naphthalene
CSOs (throughout)	Phosphorus, PCBs

Table B in Appendix A lists the correspondence between particular samples from the various cores and the sample numbers used in the analytical data tables.

In the following discussion, qualitative terms such as "low", "moderate", "high", etc., are based upon the author's experience with Great Lakes sediment data and the April 1977 EPA, Region V, "Guidelines for the Pollutional Classification of Great Lakes Harbor Sediments" (Appendix B).

CONVENTIONAL POLLUTANTS

Table C in Appendix A contains the analytical data from conventional pollutants and metals from the July 29-31, 1980 study.

Oil and Grease

Oil and grease levels were very high throughout the study area, ranging from about 4,000 to 15,000 mg/kg.

In the Milwaukee River, oil and grease levels were highest at St. Paul Avenue (15,000 mg/kg), decreasing both upstream and downstream of that point.

Oil and grease levels in the Menomonee River and Menomonee Canal were the highest in the study area, ranging up to 23,300 mg/kg. Concentrations generally decreased with distance downstream in the river and canal.

Sediment oil and grease concentrations in the upstream portion of the Kinnickinnic River were the lowest in the study area (2,420 to 4,940 mg/kg). Concentrations increased downstream and were highest in the vicinity of Kinnickinnic Avenue and in the Central Kinnickinnic Basin (15,900 and 16,400 mg/kg, respectively). Sediment oil and grease levels peaked again off of the Jones Island STP (14,400 mg/kg). This spatial variation of pollutant concentrations was found to be common of most pollutants. This pattern, shown in Figure 2, will be referred to as the "typical" pattern in the remainder of this report.

Based on the data, sources of oil and grease appear to be located on the Menomonee River at or upstream of 25th Street, on the Menomonee Canal, on the Kinnickinnic River in the area between Kinnickinnic Avenue and the Kinnickinnic Basin, and the Jones Island STP.

The high oil and grease levels on the Milwaukee River at St. Paul Avenue could be explained by three different machanisms: (a) There is a source (CSO, point source) in the vicinity of St. Paul Avenue. (b) There is an upstream source on the Milwaukee River, but the hydraulic characteristics of the Lake Michigan/Milwaukee River interaction result in a net flow minimum in the vicinity of St. Paul Avenue, resulting in the suspended contaminants from upstream settling out in this area. (c) The hydraulic characteristics of the Milwaukee River/Menomonee River/WEPCO power plant intake and discharge interaction are such that contaminated sediments originating from the Menomonee River are transported upstream into the

Milwaukee River, reaching St. Paul Avenue, where the net flow in the Milwaukee is near zero, causing high rates of deposition in that area. Such flow reversals have been found to occur (Gruber, 1981). It is most likely that the actual situation is a complex combination of all three mechanisms operating in concert.

Total Phosphorus

Phosphorus levels throughout the Estuary were very high. The typical range was from 500 to 1,500 mg/kg. The highest sediment total phosphorus levels (8,250 mg/kg) were found near the Jones Island STP, followed by the St. Paul Avenue site on the Milwaukee River (2,630 mg/kg).

Phosphorus concentrations did not follow the typical pattern of spatial variation. Phosphorus levels in all three rivers tended to increase proceeding downstream, probably due to the cumulative effects of CSO discharges. Based on the data, the primary sources of phosphorus appear to be CSOs and the Jones Island STP discharge.

Ammonia

Sediment ammonia levels in the Estuary were high, typically ranging from 200 to 400 mg/kg. The spatial distribution of ammonia concentrations followed the typical pattern (Figure 2). In the Milwaukee River, ammonia levels increased from Walnut Street to St. Paul Avenue. Ammonia levels in the Menomonee River and Menomonee Canal decreased proceeding downstream. The highest ammonia levels (1,250 mg/kg) were found in the upstream-most samples on the Menomonee River. Ammonia concentrations increased proceeding downstream on the Kinnickinnic River toward the Kinnickinnic Basin. Based on the data, the principal sources of ammonia appear to be located upstream of 25th Street on the Menomonee River; along the Menomonee Canal; in the vicinity of the Kinnickinnic Basin; and the Jones Island STP.

Total Kjeldahl Nitrogen

Total Kjeldahl nitrogen (TKN) levels were high in the Estuary, typically ranging from 1,500 to 3,000 mg/kg. The spatial distribution of sediment TKN followed the typical pattern (Figure 2). The highest TKN levels (7,680 mg/kg) were found in the samples from 25th Street on the Menomonee River.

Total Volatile Solids

Total volatile solids (TVS) levels were high, typically ranging from 10 to 15 percent. TVS levels followed the typical pattern of spatial variation (Figure 2). The highest TVS levels were in the lower half of the core from site 12 (Milwaukee River and Menomonee River confluence (19.2%)) and off of the Jones Island STP (16.8%). There is no apparent reason for the high TVS level at site 12, since levels of most other pollutants were very low at this scoured site.

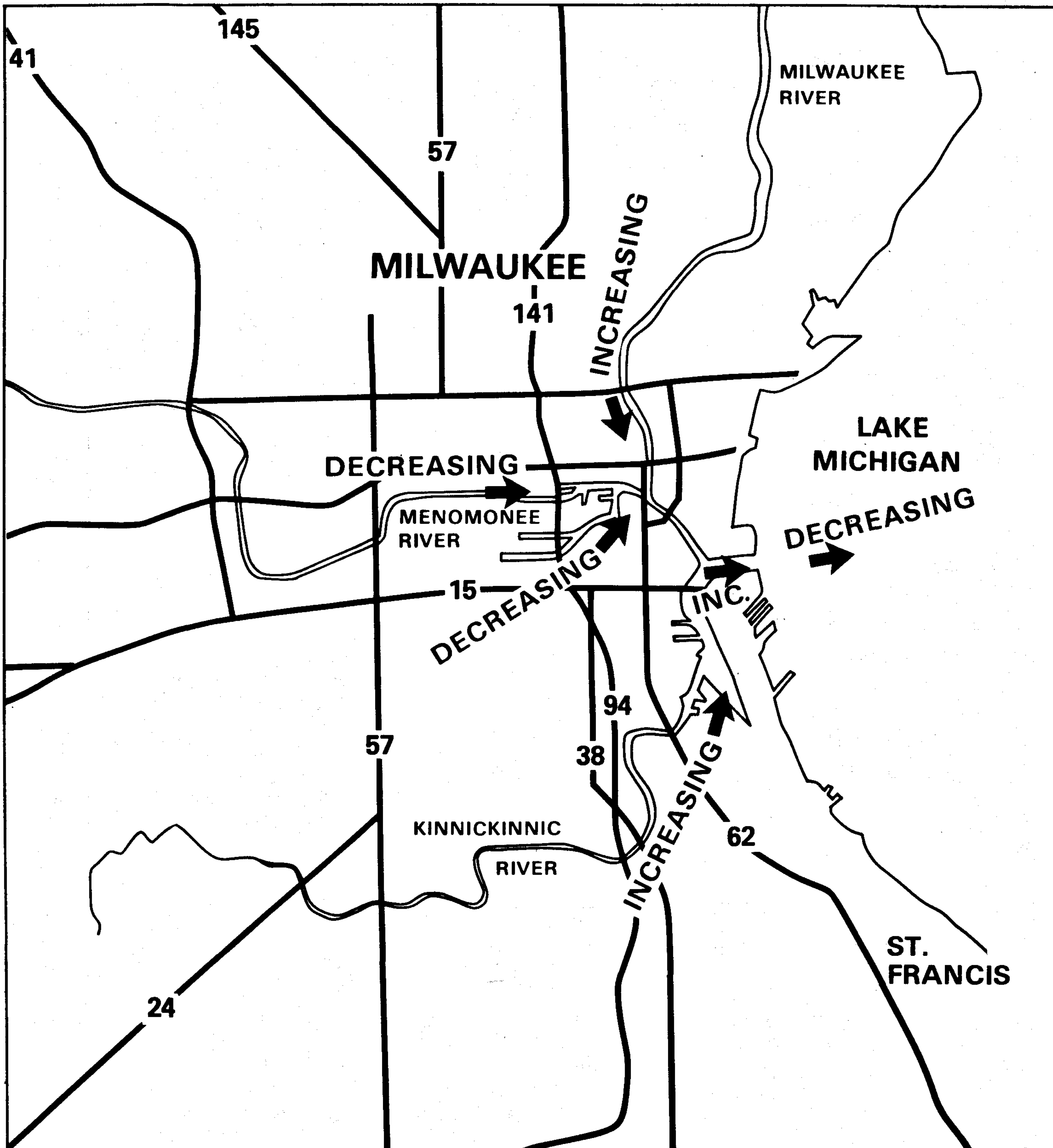

Figure 2. Typical Variation in Sediment Pollutant Concentration July 29-31, 1980

Chemical Oxygen Demand

Sediment chemical oxygen demand (COD) levels were moderate in the Estuary, typically ranging from 40,000 to 60,000 mg/kg. The highest COD levels were found at 25th Street on the Menomonee River (175,000 mg/kg) and at the Hoan Bridge in the Inner Harbor Entrance Channel (148,000 mg/kg). The pattern of COD concentration followed the typical spatial pattern (Figure 2).

Phenols

Levels of phenols typically varied from 0.2 to 0.5 mg/kg. The highest levels were found on the Menomonee River at Muskego Avenue (3.51 mg/kg) and off the Jones Island STP (2.63 mg/kg). The distribution of phenols appeared to be more random than that of the other pollutants discussed so far.

Based on the data, sources of phenols appear to be located upstream of Walnut Street on the Milwaukee River; between 25th Street and Muskego Avenue on the Menomonee River; upstream of Lincoln Avenue on the Kinnickinnic River; and at the Jones Island STP.

Cyanide

Sediment cyanide levels were an order of magnitude higher in the Central Kinnickinnic Basin (36.7 mg/kg) than the levels typical of the rest of the Estuary (3 to 5 mg/kg). Cyanide levels were lowest in the Milwaukee River and upstream of Rogers Street on the Kinnickinnic River. Intermediate cyanide levels (6 to 12 mg/kg) were found off of the Jones Island STP and upstream of 7th Street on the Menomonee River.

METALS

Sediment metals concentrations followed the typical pattern of spatial variation depicted in Figure 2.

Mercury

Sediment mercury levels in the Estuary were high, typically ranging from 0.5 to 1.0 mg/kg. The highest mercury levels were found in the Menomonee Canal (up to 2.96 mg/kg); at St. Paul Avenue on the Milwaukee River (2.39 mg/kg); and off of the Jones Island STP (2.30 mg/kg).

Lead

Sediment lead levels were very high, typically varying between 300 and 500 mg/kg. Concentrations were highest at 25th Street on the Menomonee River (1,180 mg/kg) and at Kinnickinnic Avenue on the Kinnickinnic River (1,080 mg/kg).

Cadmium

Sediment cadmium levels were high, typically ranging from 10 to 20 mg/kg. The highest cadmium levels were found off of the Jones Island STP (73.7 mg/kg), in the Central Kinnickinnic Basin (45.7 mg/kg), and at 25th Street on the Kinnickinnic River (34.4 mg/kg).

Chromium

Sediment chromium levels were very high in the Estuary, typically varying between 200 and 500 mg/kg. The highest levels were found off of the Jones Island STP (2,380 mg/kg) and at St. Paul Avenue on the Milwaukee River 2,250 mg/kg).

Arsenic

Sediment arsenic levels were very high, typically ranging from 15 to 40 mg/kg. The highest concentrations of arsenic were found in the Central Kinnickinnic Basin (69.4 mg/kg), off of the Jones Island STP (45.2 mg/kg), at 11th Street on the Menomonee Canal (44.7 mg/kg), at Muskego Avenue on the Menomonee River (42.5 mg/kg), and in the Outer Harbor (site 1) (41.8 mg/kg).

Zinc

Sediment zinc concentrations in the Estuary were high, typically ranging from 400 to 700 mg/kg. The highest zinc concentrations were observed off of the Jones Island STP (1,950 mg/kg), in the Central Kinnickinnic Basin (1,730 mg/kg), and at 25th Street on the Monomonee River (1,140 mg/kg).

Copper

Sediment copper levels were high in the Estuary, typically varying between 100 and 200 mg/kg. Copper concentrations were highest (about 300 mg/kg) at 25th Street on the Menomonee River, at 11th Street on the Menomonee Canal, in the Central Kinnickinnic Basin, and off of the Jones Island STP.

Manganese

Moderate to high levels of manganese were found in the Estuary sediments, typically varying between 400 and 700 mg/kg. The highest levels of manganese were observed in the Menonomee River from 25th Street to 7th Street (800 to 1,200 mg/kg), in the Milwaukee River between the Menomonee River junction and Florida Street (800 to 900 mg/kg), and in the Kinnickinnic River at Greenfield Avenue. In all of the areas just listed, the highest concentration of manganese were from the lower (older) sediment deposits in the core, this is in contrast with results found for most other pollutants, particularly at sites 5 and 11 (Kinnickinnic River at Greenfield Avenue and Milwaukee River at Florida Street, respectively), where surface concentrations for most other pollutants were typically much higher than those deeper in the core. Also, in contrast to other pollutants, manganese levels were high at the Milwaukee River/Menomonee River junction which is a non-depositional area. The above leads to the conclusion that the high manganese levels may be due to naturally high levels in the Estuary sediments.

Tin

Concentrations of tin in the sediments of the Estuary typically ranged from 20 to 30 mg/kg. The highest levels of tin were observed at St. Paul Avenue on the Milwaukee River (114 mg/kg), at the confluence of the Menomonee River and Canal (97.9 mg/kg), off the Jones Island STP (65 mg/kg), and at the confluence of the Menomonee and Burnham Canals (64.3 mg/kg). The pattern for tin in the Menomonee River departs from that of the typical variation. Tin levels were highest downstream in the Menomonee River/Canal junction area, whereas, for other pollutants, levels typically dropped off in that area from their upstream concentrations. This indicates a possible source of tin in the lower Menomonee River/Menomonee Canal area.

Cobalt

Cobalt levels in the Estuary sediments typically varied between 5 and 10 mg/kg. Cobalt levels at Muskego Avenue on the Menomonee River (23.8 mg/kg) are much higher than anywhere else in the Estuary, indicating a possible source of cobalt in this area.

Selenium

Sediment selenium levels were less than the laboratory's analytical detection limit of 2 mg/kg throughout the Estuary except off of the Jones Island STP (5.53 mg/kg) and in the Outer Harbor (Site 1) where selenium was just about the analytical detection limit, indicating the Jones Island STP as the most likely source of the selenium.

ORGANIC PRIORITY POLLUTANTS

Table D of Appendix A shows organic compounds that were sought and their typical detection limits. Actual detection limits varied somewhat from sample to sample depending upon levels of interferences in the particular sample for the particular compound being sought. For easier data display, the organic pollutants data (Table E of the Appendix) only shows compounds that were found at concentrations in excess of the detection limit.

Polychlorinated Biphenyls (PCBs)

Sediment PCB concentrations in the Estuary typically ranged from 2 to 5 mg/kg total PCBs. The highest PCB concentrations were found off the Jones Island STP (47 mg/kg) and at St. Paul Avenue on the Milwaukee River (32 mg/kg). The patterns for PCBs on the Menomonee River and Kinnickinnic River were different from the typical pattern of spatial variation (Figure 2).

On the Kinnickinnic River, sediment PCB concentrations were essentially constant in the study area, averaging around 5 mg/kg, with a somewhat higher concentration in the northeast corner of the Kinnickinnic Basin (10.22 mg/kg). PCB concentrations were highest at the surface. This seems to indicate a continuing, diffuse source, either nonpoint or CSO, on the Kinnickinnic River, and perhaps a source in the Kinnickinnic Basin.

On the Menomonee River, sediment PCB concentrations were low at 25th Street (1.3 mg/kg) and decreased with depth in the core, indicating the probable absence of either a present or past source upstream of that point. PCB concentrations averaged 3 to 4 mg/kg on the river, except for a rise to around 10 mg/kg in the surface sediments at 7th Street, indicating a possible localized source in that vicinity, with otherwise diffuse sources in the river.

On the Menomonee Canal, PCB concentrations increased from 5.5 mg/kg at 11th Street to 8.5 mg/kg at the junction of the Menomonee and Burnham canals. At the junction, PCB levels increased with depth, being 3 mg/kg at the surface and 8.5 mg/kg at depth, indicating past contamination from a source that has since been curtailed or eliminated.

Other Organic Priority Pollutants

Select samples were chosen for additional organic GC/MS scans (base neutral, acid, and pesticide fractions) based upon the field observations (odor, oil, color, sediment type). Those chosen were generally those that would be expected to have higher levels of contamination, the purpose being to characterize average worst-case levels of contamination in the Estuary sediments.

Pesticides

Pesticides were only detected in the area from the Outer Harbor to the Milwaukee/Kinnickinnic River confluence, and at 25th Street on the Menomonee River, and then usually only in trace amounts. The exceptions were: 1.1 mg/kg of heptachlor were detected off the Jones Island STP and 2.1 mg/kg of toxaphene-like components were detected at the Milwaukee/Kinnickinnic River confluence. The pattern suggests some pesticides contamination coming from upstream in the Menomonee River and from the Jones Island STP.

Phenolic Compounds

Phenolic compounds were not detected in the Estuary sediments except for trace amounts of 2,4-dimethylphenol at St. Paul Avenue on the Milwaukee River and at 11th Street in the Menomonee Canal, and a high concentration of pentachlorophenol (4.5 mg/kg) off the Jones Island STP. Pentachlorophenol (PCP) has been previously detected in sludge from the Jones Island STP (Milwaukee Metropolitan Sewage District, 1981).

Phthalates

Trace levels of several phthalates were detected in virtually all samples. Bis (2-ethylhexyl) phthalate (DEHP) was detected at higher concentrations, typically varying between 5 and 15 mg/kg. Levels of this phthalate were invariably highest in the surface sample from each core. The concentrations of DEHP were highest off the Jones Island STP (43 mg/kg) and at 25th Street on the Menomonee River (41.3 mg/kg). The spatial distribution of concentrations of DEHP follows the typical pattern (Figure 2).

Polynuclear Aromatic Hydrocarbons

A number of compounds in the polynuclear aromatic (PNA) group were commonly found in the sediments of the Estuary. The PNAs most frequently found at levels in excess of 10 mg/kg (a level arbitrarily chosen for convenience in aggregation of the data) and their typical concentrations in mg/kg were: Fluoroanthene (10-30), benzo(a) anthracene/chrysene (20-50), benzo(a) pyrene (5-20), 3,4-benzofluoranthene/benzo (k) fluoranthene (20-40), anthracene/phenanthrene (15-35), and pyrene (15-30). PNAs were generally highest in the upper 30 cm of the core samples. The highest concentrations of PNAs were found in the Central Kinnickinnic Basin, at Walnut Street and St. Paul Avenue on the Milwaukee River, and at 25th Street on the Menomonee River. Levels of PNAs were fairly constant on the Milwaukee River from Walnut Street to St. Paul Avenue, indicating a source upstream and/or a diffuse source such as CSOs. In the Menomonee River, PNAs were highest at 25th Street and decreased steadily downstream, indicating a source at or upstream of 25th Street. Levels of PNAs were fairly low on the Menomonee Canal. PNA levels were low at Lincoln Avenue on the Kinnickinnic River, then increased from Kinnickinnic Avenue to the Central Kinnickinnic Basin, indicating a possible source in that vicinity.

Others

Chlorinated benzene priority pollutants were not detected in the Estuary sediments except for traces of 1,3 - and 1,4-dichlorobenzene at the Menomonee River/Canal confluence.

Traces of N-nitrosodiphenylamine were found in the Central Kinnickinnic Basin. Traces of 3,3-dichlorobenzidine were found at 25th Street on the Menomonee River.

Elevated levels of naphthalene were found in the sediments of the Central Kinnickinnic Basin (9.22 to 24.3 mg/kg). Levels of napthalene at other locations were low (up to 1 or 2 mg/kg) or nondetectable. There appears to be a source of naphthalene in the Kinnickinnic Basin area.

Off of Jones Island STP, 4.3 mg/kg of 2,4-dinitrotoluene was found.

IV. COMPARISON WITH HISTORICAL SEDIMENT DATA

Sediments in the Estuary were sampled during the summer of 1977 by Rexnord (Rexnord, 1977). Core samples were obtained and analyzed in halves or thirds for total solids, total volatile solids, COD, ammonia, total phosphorus, cadmium, zinc, lead, copper, BOD_5, nitrate + nitrite, density, iron, redox, and pH.

Comparison of data from comparable locations shows results for ammonia, total phosphorus, cadmium, copper, zinc, and lead to be comparable between the 1977 and 1980 surveys. However, levels of total volatile solids in the 1980 survey were two to three times higher than the 1977 levels; and COD levels for the 1980 survey were only about half of what was found in 1977. These differences are most likely due to differences in analytical methods used in the two sets of analyses rather than an actual change in pollutant conditions, since levels of the other pollutants were little changed between the two surveys.

The 1977 study concluded that there were no consistent patterns in pollutant concentrations with depth. In contrast, the 1980 data showed that most contaminants were higher in the upper portions of the cores. This difference may be due to differences in the length of cores obtained in the two surveys as well as differences in the size of the vertical sections (slices) analyzed.

The 1977 report concluded that levels of pollutants in sediments were similar in all three rivers of the Estuary, except for zinc and lead which were two to three times higher in the Kinnickinnic River than in the other two rivers. The 1980 data generally shows the Menomonee River has the highest overall sediment pollutant levels, the Kinnickinnic River has the lowest, while the Milwaukee River is intermediate between the two.

PCBs

The most comprehensive previous sediment sampling for PCBs in the area was conducted from May 1975 to April 1976 by the Wisconsin Department of Natural Resources (Wawrzyn et. al., undated). That study included the Milwaukee and Kinnickinnic Rivers, but not the Menomonee River. Surface grab samples were obtained and analyzed for PCBs and metals.

A comparison of PCB results from comparable sampling sites shows very little difference between the 1975/1976 study (surface grab sample) results and the 1980 (core sample) maximum values. This is because the highest PCB levels in the 1980 study were found at the surface (within the top 30 or 60 cm of the cores) on the Milwaukee and Kinnickinnic Rivers.

Surface grab sediment samples were taken in the Kinnickinnic Basin and the Outer Harbor on March 4, 1980 for a Milwaukee Harbor Commission dredging permit application. The PCB analyses (Sommer-Frey Laboratories, Inc.) showed high levels of PCBs (55.6 and 73.3 mg/kg) in the two samples from the Kinnickinnic Basin and in one sample (38 mg/kg) from a mooring slip (South Slip No. 2) in the Outer Harbor about 2,500' south of the Inner Harbor Entrance Channel.

Due to the regulatory implications for disposal of dredge spoil contaminated with such high levels of PCBs, the Harbor Commission had the areas re-sampled on October 27-29, 1980 by the University of Wisconsin, Great Lakes Research Facility. The University obtained core samples and sectioned them in 10 cm vertical sections. The analyses (Raltech Scientific Services) substantiated the elevated levels in the Outer Harbor (up to 91.5 mg/kg PCBs), but did not substantiate the levels found in the Kinnickinnic Basin in the earlier study, finding a maximum of 33.5 mg/kg PCBs in a single 10 cm segment of one core sample. It is unknown why there was such a large discrepancy between the two sets of samples in the Kinnickinnic Basin. It should be noted that the USEPA July 29-31, 1980 study results agree with the October 27-29, 1980 University of Wisconsin study results for the Kinnickinnic Basin samples when the difference in vertical segmentation of samples is taken into account.

The Milwaukee Metropolitan Sewerage District (MMSD) obtained sediment core samples at 8 locations in the vicinity of the Jones Island STP outfall on June 20, 1980. The cores were analyzed for PCBs in halves or thirds. Concentrations were in the range of 10 to 25 mg/kg total PCBs and tended to be higher in the upper halves of the cores. The highest concentration (79.2 mg/kg) was found in the lower half of the core off of South Slip No. 1. The results of the MMSD survey agree with those of the USEPA July 29-31, 1980 study.

Other Organic Priority Pollutants

The author was not aware of any comprehensive previous sediment surveys for organic priority pollutants other than PCBs in the Estuary.

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APPENDIX A

FIELD OBSERVATIONS AND CHEMISTRY DATA

from July 29-31, 1980

U.S. ENVIRONMENTAL PROTECTION AGENCY

Milwaukee Estuary Sediment Study

Table A Boring Log

Kinnickinnic, Menomonee, and Milwaukee Rivers

Sampling Dates: July 29, 30, and 31
July 29 station No. 10, 14, 15, and 16
July 30 station No. 1-9
July 31 station No. 11, 12, 17-23

Sampling Equipment
Benthos Gravity Corer Model 2171
Wildco #1725 G10 Grab Sampler

Weather Conditions
July 29 sunny
July 30 rain
July 31 overcast to partly cloudy

There is a possibility of atmospheric contamination on July 30, 1980 due to high winds and visible particulates.

Station No. 1

Depth of Water: 30 ft
Length of Core: 15 cm
Sediment: hard clay
Color: grey
Odor: —

Station No. 2

Depth of Water: 28 ft
Length of Core: 85 cm
Sediment: mud over clay
Color: mud—dark grey to black; clay—grey
Odor: stale

Station No. 3

Depth of Water: 29 ft
Length of Core: 25 cm
Sediment: mud with a little organic debris
Color: dark grey to black
Odor: earthy

Station No. 4

Depth of Water: 28 ft
Length of Core: 60 cm
Sediment: mud
Color: dark grey to black
Odor: earthy

Station No. 5

Depth of Water: 30 ft
Length of Core: 75 cm
Sediment: mud over clay
Color: mud--black; clay--grey
Odor: hydrocarbons

Sediment contained a little oil. The corer stopped in a hard clay layer.

Station No. 6

Depth of Water: 28 ft
Length of Core: 110 cm
Sediment: mud
Odor: oily, hydrocarbons
Color: black

Station No. 7a

Depth of Water: 28 ft
Length of Core: 60 cm
Sediment: mud
Color: dark grey to black
Odor: oily

Station No. 7b
Depth of water: 28 ft
Length of Core: 55 cm
Sediment: mud
Color: dark grey to black
Odor: oily

Station No. 8

Depth of Water: 27 ft
Length of Core: 60 cm
Sediment: mud
Color: dark grey to black
Odor: oily

Station No. 9

Depth of Water: 18 ft
Length of Core: 45 cm
Sediment: mud
Color: dark grey to black
Odor: earthy

Station No. 10

Depth of Water: 4 ft
Grab Sample
Sediment: mud
Color: black
Odor: earthy

Station No. 11a and 11b
Depth of Water: 30 ft
Length of Core: 11a--80 cm; 11b--110 cm
Sediment: mud over clay
Color: mud--black; clay--grey
Odor: oily

Station No. 12
Depth of Water: 28 ft
Length of Core: 54 cm
Sediment: clay
Color: grey
Odor: none

Station No. 13
Depth of Water: 30 ft
Length of Core: 85 cm
Sediment: mud over sandy mud
Color: black
Odor: oily

Station No. 14

Depth of Water: 10 ft
Grab Sample
Sediment: mud
Color: dark grey
Odor: earthy

Station No. 15

Depth of Water: 20 ft
Grab Sample
Sediment: mud with some organic debris
Color: dark grey to black
Odor: earthy

Station No. 16

Depth of Water: 12-24 ft
Grab Sample
Sediment: organic debris (leaves and twigs); also some muddy sand, gravel
Odor: earthy to peaty
Number of Attempts: 9

Station No. 17
Depth of Water: 28 ft
Length of Core: 90 cm
Sediment: mud over clay
Color: mud--black; clay--grey
Odor: oily, disagreeable

Station No. 18

Depth of Water: 25 ft
Length of Core: 96 cm
Sediment: mud with some oil
Color: black
Odor: hydrocarbons, disagreeable

Station No. 19

Length of Core: 120 cm
Sediment: mud over clay
Color: mud--black; clay--grey
Odor: hydrocarbons, disagreeable

Station No. 20
Length of Core: 25 cm
Sediment: mud over clay
Color: mud--black; clay--grey
Odor: hydrocarbons

Sample could not be taken where indicated on map due to a bridge that would not open. Sample was taken roughly one block downstream.

Station No. 21
Depth of Water: 28 ft
Length of Core: 115 cm
Sediment: mud over clay
Color: mud--black; clay--grey
Odor: hydrocarbons, disagreeable

Station No. 22
Length of Core: 85 cm
Sediment: mud, oily
Color: black
Odor: hydrocarbons, disagreeable

Station No. 23
Depth of Water: 14 ft
Length of Core: 100 cm
Sediment: mud with top covering of organic matter
Color: black
Odor: hydrocarbons, very disagreeable

Table B Sample Numbers Used in this Report and the Sampling Location and Depth Interval They Represent.

Sample Number	Sampling Location	Depth Interval in Core (cm)
1a	1	0-15
2a	2	0-30
2b	2	30-60
2c	2	60-85
3a	3	0-25
4a	4	0-30
4b	4	30-60
5a	5	0-30
5b	5	30-60
5c	5	60-75
6a	6	0-30
6b	6	30-60
6c	6	60-90
6d	6	90-110
7a	7	0-30
7b	7	30-60
7rep.a	7 Replicate	0-30
7rep.b	7 Replicate	30-50
8a	8	0-30
8b	8	30-60
9a	9	0-30
9b	9	30-45
10	10	Grab
11a	11	0-30
11b	11	30-60
11c	11	60-80
11rep.a	11 Replicate	0-30
11rep.b	11 Replicate	30-60
11rep.c	11 Replicate	60-90
11rep.d	11 Replicate	90-110
12a	12	0-30
12b	12	30-54

Table B Continued

13a	13	0-30
13b	13	30-60
13c	13	60-85
15	15	Grab
17a	17	0-30
17b	17	30-60
17c	17	60-90
18a	18	0-30
18b	18	30-60
18c	18	60-90
18d	18	90-96
19a	19	0-30
19b	19	30-60
19d	19	90-120
21a	21	0-30
21b	21	30-60
21c	21	60-90
21d	21	90-115
22a	22	0-30
22b	22	30-60
22c	22	60-85
23a	23	0-30
23b	23	30-60
23c	23	60-90
23d	23	90-100

Table C Sediment Concentrations of Some Conventional Pollutants and Metals in the Milwaukee Harbor Estuary July 29-31,1980. (All values are mg/kg dry weight unless noted otherwise.)

Parameter	Sample Number						
	1a	2a	2b	2c	3a	4a	4b
Total Solids (%)	73.4	30.0	34.4	53.3	34.2	36.1	44.0
Total Volatile Solids (%)	1.6	14.4	16.8	7.6	10.4	10.6	11.0
Chemical Oxygen Demand	6,800	51,900	65,400	35,200	148,000	46,500	44,600
Total Kjeldahl Nitrogen	313	1,680	2,320	975	4,420	1,520	1,100
Ammonia Nitrogen	198	312	460	272	278	82	288
Total Phosphorus	565	5,470	8,250	1,530	141	1,720	2,080
Oil and Grease	<1,000	11,400	14,400	7,310	6,240	6,330	7,270
Mercury	0.10	0.83	2.30	1.22	0.15	0.58	0.66
Lead	23.2	252	407	110	423	335	321
Zinc	80.9	592	1,950	657	423	576	554
Manganese	392	293	524	436	667	511	503
Cobalt	10.6	5.4	10.5	5.4	1.6	7.7	6.9
Arsenic	41.8	6.70	45.2	14.3	17.8	33.2	12.4
Cadmium	10.1	25.8	73.7	20.7	11.1	8.4	8.4
Chromium	91.0	1,600	2,380	835	482	616	690
Copper	22.2	108	293	93.0	105	90.0	103
Cyanide	0.92	4.84	5.88	3.20	<2.0	2.43	2.33
Selenium	2.34	5.53	2.05	<2.0	<2.0	<2.0	<2.0
Tin	4.0	19	65	12.4	18.9	10.5	12.6
Phenols	0.44	1.23	2.63	0.44	0.70	1.72	0.36

Table C Sediment Concentrations of Some Conventional Pollutants and Metals in the Milwaukee Harbor Estuary July 29-31,1980. (All values are mg/kg dry weight unless noted otherwise.)

Parameter	Sample Number						
	5a	5b	5c	6a	6b	6c	6d
Total Solids (%)	47.1	57.1	56.5	43.8	43.6	45.6	52.4
Total Volatile Solids (%)	8.6	6.7	4.3	12.6	14.5	14.8	12.4
Chemical Oxygen Demand	71,500	10,900	14,000	68,600	88,000	97,200	63,600
Total Kjeldahl Nitrogen	1,800	1,160	1,110	1,350	1,370	2,650	2,400
Ammonia Nitrogen	202	254	334	336	438	360	372
Total Phosphorus	386	639	533	1,740	1,160	1,130	954
Oil and Grease	5,460	<1,000	<1,000	6,470	16,400	14,700	7,700
Mercury	0.92	0.16	<0.1	1.48	1.83	1.92	2.05
Lead	392	89	30	534	436	477	324
Zinc	582	106	74	925	1,040	1,730	730
Manganese	639	778	859	598	409	425	478
Cobalt	5.6	2.4	0.9	8.5	2.0	7.2	7.2
Arsenic	16.7	12.8	5.7	40.6	38.2	69.4	61.4
Cadmium	13.7	5.8	5.4	17.8	19.4	45.7	14.7
Chromium	322	15	36	386	330	423	355
Copper	110	33	25	154	192	271	140
Cyanide	2.95	<1.8	<1.7	12.6	18.3	36.7	15.5
Selenium	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Tin	14.2	<8.0	<8.0	25.0	19.6	23.2	17.6
Phenols	0.13	0.12	0.39	0.14	0.34	0.46	0.29

Table C Sediment Concentrations of Some Conventional Pollutants and Metals in the Milwaukee Harbor Estuary July 29-31,1980. (All values are mg/kg dry weight unless noted otherwise.)

Parameter	Sample Number							
	7a	7b	7rep.a	7rep.b	8a	8b	9a	9b
Total Solids (%)	49.6	62.4	37.9	68.7	46.3	51.5	67.2	58.
Total Volatile Solids (%)	9.4	8.4	10.8	6.1	10.5	11.1	7.0	10.
Chemical Oxygen Demand	46,400	31,700	53,300	21,900	44,300	41,900	21,500	41,60
Total Kjeldahl Nitrogen	1,230	966	1,480	450	1,490	656	632	1,640
Ammonia Nitrogen	151	152	219	96	244	262	177	463
Total Phosphorus	1,080	561	1,730	358	890	604	726	1,060
Oil and Grease	3,800	3,800	10,100	2,000	12,600	15,900	2,420	4,940
Mercury	0.83	0.86	1.09	0.66	0.47	0.63	0.40	0.77
Lead	298	160	417	127	838	1,080	659	500
Zinc	595	276	676	165	919	999	564	664
Manganese	500	265	427	223	643	601	388	470
Cobalt	5.7	3.21	7.69	3.52	5.8	8.11	5.3	7.37
Arsenic	21.0	17.3	35.0	8.8	13.6	28.5	14.4	12.0
Cadmium	11.6	6.2	13.4	5.1	12.8	14.7	7.1	13.3
Chromium	234	156	290	136	140	152	64	87
Copper	94	69	129	40	150	137	111	114
Cyanide	3.95	5.08	4.49	6.43	3.67	<1.9	<1.5	3.24
Selenium	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Tin	<8.0	<8.0	35.5	<8.0	48.1	40.8	10.6	23.2
Phenols	0.20	0.14	0.24	0.07	0.65	0.49	0.52	0.45

Table C   Sediment Concentrations of Some Conventional Pollutants and Metals in the Milwaukee Harbor Estuary July 29-31,1980. (All values are mg/kg dry weight unless noted otherwise.)

Parameter	Sample Number							
	10	11a	11b	11c	11rep.a	11rep.b	11rep.c	11rep.d
Total Solids (%)	66.9	37.8	69.0	59.2	51.1	63.1	57.7	56.3
Total Volatile Solids (%)	3.5	12.2	4.0	5.2	6.2	4.6	5.1	5.0
Chemical Oxygen Demand	19,000	38,600	12,500	19,000	28,400	15,200	19,900	18,000
Total Kjeldahl Nitrogen	<220	1,530	1,020	1,220	1,470	1,140	1,200	927
Ammonia Nitrogen	176	280	146	164	219	184	218	243
Total Phosphorus	386	1,670	393	512	1,510	525	693	696
Oil and Grease	3,980	7,900	<1,000	<1,000	2,960	998	<1,000	<1,000
Mercury	0.21	0.70	<0.09	<0.1	0.37	<0.1	<0.1	<0.1
Lead	608	467	28	34	277	37	44	40
Zinc	419	485	70	77	343	60	85	94
Manganese	429	590	537	798	691	709	819	831
Cobalt	3.73	6.73	2.12	3.59	4.39	2.71	5.56	4.00
Arsenic	4.2	6.9	0.8	1.8	12.0	4.0	1.5	3.6
Cadmium	9.6	11.6	<1.00	<1.00	5.33	<1.00	<1.00	<1.00
Chromium	54	424	17	20	355	22	28	43
Copper	77	121	17	21	80	18	23	27
Cyanide	<1.5	<2.5	<1.4	<1.6	<1.9	<1.6	<1.7	<1.7
Selenium	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Tin	21.5	32.6	<8.0	<8.0	<8.0	<8.0	<8.0	<8.0
Phenols	1.27	0.16	<0.06	0.76	0.94	0.51	0.68	0.73

Table C Sediment Concentrations of Some Conventional Pollutants and Metals in the Milwaukee Harbor Estuary July 29-31,1980. (All values are mg/kg dry weight unless noted otherwise.)

Parameter	Sample Number					
	12a	12b	13a	13b	13c	15
Total Solids (%)	57.6	65.3	36.0	37.7	49.4	39.6
Total Volatile Solids (%)	6.6	19.2	9.9	12.2	10.1	8.8
Chemical Oxygen Demand	27,000	21,600	38,500	48,200	56,800	46,100
Total Kjeldahl Nitrogen	1,110	1,290	2,000	3,150	2,000	2,740
Ammonia Nitrogen	56	104	164	257	186	172
Total Phosphorus	677	492	2,120	2,630	1,410	1,300
Oil and Grease	<1,000	<1,000	8,420	15,000	8,060	12,200
Mercury	<0.1	<0.09	1.39	2.39	1.88	0.61
Lead	36	38	727	636	533	562
Zinc	90	73	642	732	661	406
Manganese	801	892	738	579	537	431
Cobalt	3.32	3.60	4.87	6.20	5.77	3.90
Arsenic	5.3	2.7	14.1	20.6	25.3	17.7
Cadmium	<1.00	<1.00	7.28	9.26	7.18	4.15
Chromium	18	27	1,080	2,250	311	130
Copper	23	22	165	226	207	117
Cyanide	<1.6	<1.5	<2.6	<1.6	<2.0	<2.5
Selenium	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Tin	<8.0	<8.0	64.6	114	66.9	8.8
Phenols	0.52	0.76	0.22	0.32	0.26	1.56

Table C Sediment Concentrations of Some Conventional Pollutants and Metals in the Milwaukee Harbor Estuary July 29-31,1980. (All values are mg/kg dry weight unless noted otherwise.)

Parameter	Sample Number						
	17a	17b	17c	18a	18b	18c	18d
Total Solids (%)	51.4	57.8	54.6	44.6	50.6	57.0	55.8
Total Volatile Solids (%)	7.8	11.8	9.1	9.3	8.4	10.0	8.3
Chemical Oxygen Demand	37,600	49,600	39,900	47,300	43,800	55,000	102,000
Total Kjeldahl Nitrogen	1,090	1,910	2,800	1,980	1,940	2,300	2,810
Ammonia Nitrogen	185	223	253	215	302	240	265
Total Phosphorus	1,260	1,530	1,160	1,460	1,410	768	366
Oil and Grease	6,530	<1,000	1,960	5,230	6,070	7,960	10,050
Mercury	0.66	1.06	0.56	0.82	1.00	1.24	2.57
Lead	529	349	310	448	448	370	395
Zinc	322	509	426	564	554	528	605
Manganese	402	578	668	625	599	497	460
Cobalt	8.77	6.62	5.81	5.54	6.24	5.51	6.29
Arsenic	11.6	24.4	15.6	19.3	19.6	21.5	26.6
Cadmium	10.9	11.4	8.27	10.2	7.45	7.44	6.75
Chromium	267	298	227	411	445	405	461
Copper	120	174	150	217	187	168	156
Cyanide	3.21	3.34	2.38	2.20	2.65	<1.8	<1.8
Selenium	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Tin	35.1	97.9	30.6	49.1	64.3	17.4	49.1
Phenols	0.19	0.28	0.22	0.27	0.18	0.25	0.30

Table C Sediment Concentrations of Some Conventional Pollutants and Metals in the Milwaukee Harbor Estuary July 29-31,1980. (All values are mg/kg dry weight unless noted otherwise.)

Parameter	Sample Number						
	19a	19b	19d	21a	21b	21c	21d
Total Solids (%)	36.4	42.2	54.3	43.4	49.8	57.2	55.1
Total Volatile Solids (%)	10.5	14.9	8.9	9.3	9.6	7.0	6.3
Chemical Oxygen Demand	84,500	76,600	36,500	25,900	45,300	80,900	84,800
Total Kjeldahl Nitrogen	4,040	3,390	1,500	4,100	2,450	1,080	2,270
Ammonia Nitrogen	511	386	381	228	319	248	210
Total Phosphorus	591	829	285	440	1,070	350	281
Oil and Grease	19,400	8,630	1,830	10,500	15,300	10,200	<1,000
Mercury	1.06	2.96	0.60	1.00	0.80	0.66	<0.1
Lead	521	487	173	616	604	495	59
Zinc	711	793	330	702	621	472	86
Manganese	668	808	735	550	506	684	1,220
Cobalt	8.11	6.70	3.61	8.40	9.46	3.66	6.17
Arsenic	38.1	44.7	37.9	10.0	11.8	31.0	7.80
Cadmium	11.7	19.1	9.72	21.4	15.3	13.8	8.63
Chromium	521	543	167	425	531	369	43
Copper	282	216	86	121	178	144	19
Cyanide	4.04	<2.0	<1.8	<2.3	4.92	2.36	<1.8
Selenium	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Tin	13.2	25.5	<8.0	19.2	<8.0	12.6	<8.0
Phenols	0.22	0.36	0.17	0.37	0.32	0.33	0.33

Table C Sediment Concentrations of Some Conventional Pollutants and Metals in the Milwaukee Harbor Estuary July 29-31,1980. (All values are mg/kg dry weight unless noted otherwise.)

Parameter	Sample Number						
	22a	22b	22c	23a	23b	23c	23d
Total Solids (%)	47.9	60.2	63.5	33.8	41.4	48.5	46.0
Total Volatile Solids (%)	9.6	12.1	13.4	13.2	13.8	11.1	12.1
Chemical Oxygen Demand	45,600	42,400	45,600	59,900	51,900	175,000	67,600
Total Kjeldahl Nitrogen	3,850	1,840	2,660	7,680	6,500	870	1,690
Ammonia Nitrogen	242	312	431	1,250	471	645	452
Total Phosphorus	720	498	480	1,390	1,230	1,170	1,400
Oil and Grease	11,100	10,500	9,980	16,200	14,800	8,570	23,300
Mercury	0.74	0.72	2.06	0.90	0.52	0.80	1.45
Lead	665	584	479	729	683	810	1,180
Zinc	637	568	544	775	569	777	1,140
Manganese	588	823	538	815	754	715	914
Cobalt	23.8	23.8	2.86	3.50	4.85	6.56	4.25
Arsenic	18.4	42.5	24.6	17.0	3.00	16.4	15.1
Cadmium	15.7	21.6	16.6	34.4	25.1	17.5	25.2
Chromium	214	147	227	199	154	208	270
Copper	159	153	199	188	228	247	307
Cyanide	7.72	6.16	4.80	11.5	8.33	6.58	9.87
Selenium	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Tin	8.9	18.8	23.2	10.8	10.0	14.4	31.6
Phenols	0.51	3.51	0.67	0.86	1.79	0.31	0.26

Table D Organic Compounds Sought and Typical Detection Limits. (Actual detection limits for individual samples may vary as a function of interferences present, aliquot size, degree of pre-concentration, etc.)

Compound	Typical Detection Limit (mg/kg)
Pesticides	
aldrin	0.01
dieldrin	.0.01
chlordane	0.01
4,4'-DDT	0.03
4,4'-DDE	0.01
4,4'-DDD	0.01
alpha-endosulfan	0.01
beta-endosulfan	0.01
endrin	0.02
heptachlor	0.01
heptachlor epoxide	0.01
alpha-BHC	0.01
beta-BHC	0.01
gamma-BHC	0.01
delta-BHC	0.01
PCB-1242	0.01
PCB-1254	0.01
PCB-1221	0.01
PCB-1232	0.01
PCB-1248	0.01
PCB-1260	0.01
PCB-1016	0.01
toxaphene	0.01
Acid Compounds	
2,4,6-trichlorophenol	0.1
p-chloro-m-cresol	0.1
2-chlorophenol	0.1
2,4-dichlorophenol	0.1
2,4-dimethylphenol	0.1
2-nitrophenol	0.1
4-nitrophenol	0.1
2,4-dinitorphenol	1.0
4,6-dinitro-o-cresol	0.2
pentachlorophenol	0.1

Table D Continued

<u>Base/Neutral Compounds</u>

acenaphthene	0.5
benzidine	2
1,2,4-trichlorobenzene	0.1
hexachlorobenzene	0.1
hexachloroethane	0.1
bis(2-chloroethyl)ether	0.1
1,2-dichlorobenzene	0.1
1,3-dichlorobenzene	0.1
1,4-dichlorobenzene	0.1
3,3'-dichlorobenzidine	0.1
2,4-dinitrotoluene	0.2
2,6-dinitrotoluene	0.1
1,2-diphenylhydrazine (as azobenzene)	0.1
fluoroanthene	0.1
4-chlorophenyl phenyl ether	0.1
4-bromophenyl phenyl ether	0.1
bis(2-chloroisopropyl)ether	0.1
bis(2-chloroethoxy)methane	0.1
hexachlorobutadiene	0.1
hexachlorocyclopentadiene	0.1
isophorone	0.1
naphthalene	0.5
nitrobenzene	0.1
N-nitrosodiphenylamine	0.1
N-nitrosodi-n-propylamine	0.1
bis(2-ethylhexyl)phthalate	0.1
butyl benzyl phthalate	0.1
di-n-butyl phthalate	0.1
di-n-octyl phthalate	0.1
diethyl phthalate	0.1
dimethyl phthalate	0.1
benzo(a)anthracene/chrysene	0.1
benzo(a)pyrene	0.5
3,4-benzofluoranthene/benzo(k)fluoranthene	0.5
acenaphthylene	0.5
anthracene/phenanthrene	0.5
benzo(ghi)perylene	0.5
fluorene	0.5
dibenzo(a,h)anthracene	0.5
indeno(1,2,3-cd)pyrene	0.5
pyrene	0.5
2,3,7,8-tetrachlorodibenzo-p-dioxin	0.1

Table E Sediment Concentrations of Some Organic Pollutants in the Milwaukee Harbor Estuary July 29-31, 1980. (All values are mg/kg dry weight)

Parameter	Sample Number 1a	2a	2b	2c	3a*	4a	4b
aldrin		0.06					0.07
dieldrin			0.01				
chlordane		0.44					
endrin			0.03				
4,4'-DDE				0.33			
alpha-BHC			0.02	0.02			
heptachlor	0.02	0.18	1.10	0.19		0.20	0.25
gamma-BHC	0.01	0.03	0.06	0.02		0.01	0.03
delta-BHC		0.11		0.12		0.08	0.12
pentachlorophenol				4.6			
Aroclor 1254	0.40	3.50	14.0	6.20	<0.4	4.00	5.40
Aroclor 1248	0.66	4.90	33.0	7.40	<0.5	4.10	8.70
Total PCBs	1.06	8.40	47.0	13.60	<0.9	8.10	14.10
toxaphene						2.10	
2,4-dinitrotoluene			4.3				
fluoroanthene	1.1	13	11	1.4		7.0	6.0
bis(2-ethylhexyl)phthalate	0.7	43	28	8.5		11	9.6
di-n-butyl phthalate	0.3	1.2		0.7			
diethyl phthalate		1.5		0.7			
benzo(a) anthracene/ chrysene	0.7	11	9.3	2.8		6.7	5.4
benzo(a) pyrene		17	12	3.0		6.5	22
anthracene/phenanthrene		0.5					
phenanthrene		3.2	3.3	0.6		1.8	1.6
indeno(1,2,3-cd) pyrene		3.5	0.7	0.7		3.6	1.8
pyrene		13	12			7.5	6.5
fluorene			0.9				

*only analyzed for PCBs.

Table E Sediment Concentrations of Some Organic Pollutants in the Milwaukee Harbor Estuary July 29-31, 1980. (All values are mg/kg dry weight)

Parameter	Sample Number						
	5a*	5b*	5c*	6a	6b	6c	6d
Aroclor 1242	0.5						
Aroclor 1254	0.7	0.49	0.06	2.67	1.50	0.81	0.09
Aroclor 1221	1.0						
Aroclor 1232	1.0						
Aroclor 1248	5.7	1.19	0.08	2.92		0.51	0.09
Total PCBs	8.9	1.68	0.14	5.59	1.50	1.32	0.18
acenaphthene					1.06	4.01	2.01
fluoroanthene				23.2	42.5	66.9	30.4
N-nitrosodiphenylamine							0.6
naphthalene				5.68	12.7	24.3	9.22
bis(2-ethylhexyl) phthalate				5.99	3.32		
di-n-butyl phthalate				0.36			
diethyl phthalate				0.33			
benzo(a) pyrene				12.4	23.1	41.3	17.2
3,4 benzofluoranthene/ benzo (k) fluoranthene				25.0	39.1	50.9	25.2
benzo (a)anthracene/ chrysene				25.7	48.8	76.9	40.9
acenaphthylene				1.22	1.89	4.34	2.28
anthracene/phenanthrene				15.3	24.3	34.9	20.4
benzo(ghi) perylene				7.27	13.7	22.3	8.78
fluorene				0.90	2.21	2.98	1.77
dibenzo(a,h) anthracene				5.67	11.6	20.6	10.9
indeno(1,2,3-cd) pyrene				7.47	15.1	21.8	9.67
pyrene				15.6	28.5	48.1	22.9

*only analyzed for PCBs.

Table E Sediment Concentrations of Some Organic Pollutants in the Milwaukee Harbor Estuary July 29-31, 1980. (All values are mg/kg dry weight)

Parameter	Sample Number							
	7a*	7b*	7rep.a*	7rep.b*	8a	8b	9a*	9b*
Aroclor 1254	8.40			<0.03			<0.6	<0.6
Aroclor 1248	1.82	0.37	6.09	<0.04	4.86	4.05	<0.8	<0.7
Total PCBs	10.22	0.37	6.09	<0.07	4.86	4.05	<1.4	<1.3
fluoroanthene					48.4	25.3		
acenaphthene					2.84	1.19		
naphthalene					0.61	0.24		
bis(2-ethylhexyl) phthalate					8.14	2.52		
butyl benzyl phthalate					0.97	0.45		
di-n-butyl phthalate					0.32	0.17		
di-n-octyl phthalate					0.52			
diethyl phthalate					0.53			
benzo(a) pyrene					28.3	11.5		
3,4 benzofluoranthene/ benzo(k) fluoranthene					31.1	15.2		
benzo(a) anthracene/ chrysene					60.2	28.4		
acenaphthylene					0.81	0.43		
anthracene/phenanthrene					25.5	15.7		
benzo(ghi) perylene					6.75	4.23		
fluorene					2.01	1.46		
dibenzo(a,h) anthracene					6.04	3.39		
indeno(1,2,3-cd) pyrene					8.59	5.23		
pyrene					35.3	20.0		

*only analyzed for PCBs

Table E Sediment Concentrations of Some Organic Pollutants in the Milwaukee Harbor Estuary July 29-31, 1980. (All values are mg/kg dry weight)

Parameter	Sample Number 10	11a*	11b*	11c*	11 rep.a*	11 rep.b*	11 rep.c*	11 rep.d*
Aroclor 1248	5.06	5.10	0.11	0.05	4.7	0.41	0.15	0.07
Total PCBs	5.06	5.10	0.11	0.05	4.7	0.41	0.15	0.07
acenaphthene	0.32							
fluoranthene	8.02							
diethyl phthalate	0.26							
benzo(a) pyrene	2.23							
3,4-benzofluoranthene/ benzo(k) fluoranthene	3.32							
benzo(a) anthracene/ chrysene	9.40							
acenaphthylene	0.11							
anthracene/phenanthrene	5.41							
benzo(ghi) perylene	1.11							
fluorene	0.48							
benzo(a,h) anthracene	0.70							
indeno(1,2,3-cd)pyrene	1.19							
pyrene	7.96							

*only analyzed for PCBs.

Table E Sediment Concentrations of Some Organic Pollutants in the Milwaukee Harbor Estuary July 29-31, 1980. (All values are mg/kg dry weight)

Parameter	Sample Number							
	12a*	12b*	13a	13b	13c	15		
Aroclor 1248	0.04	0.07	22	32	2.1	8.8		
Total PCBs	0.04	0.07	22	32	2.1	8.8		
2,4-dimethylphenol				0.41				
acenaphthene			2.58	0.78	0.88	2.47		
fluoroanthene			46.0	29.2	15.4	64.7		
naphthalene			2.09	0.45	0.92	0.70		
butyl benzyl phthalate						0.55		
bis(2-ethylhexyl) phthalate			16.7	6.55	1.56	8.94		
di-n-butyl phthalate			0.85	0.16	0.17	0.80		
diethyl phthalate			1.03	0.29	0.88	1.34		
di-n-octyl phthalate						0.26		
benzo(a) pyrene			22.4	12.8	5.42	19.1		
~~3,4-benzofluoranthene/~~ benzo(k) fluoranthene			37.4	21.3	7.72	31.8		
~~benzo (a) anthracene/~~ chrysene			78.3	46.5	21.6	82.9		
acenaphthylene			0.52	0.54	0.46	0.56		
anthracene/phenanthrene			21.6	15.5	11.8	36.2		
benzo(ghi) perylene			7.93	8.64	2.29	7.78		
fluorene			2.44	1.11	1.21	2.64		
dibenzo(a,h) anthracene			5.61	5.79	1.39	6.25		
indeno(1,2,3-cd) pyrene			8.13	5.76	2.55	8.96		
pyrene			38.1	23.5	10.2	48.9		

*only analyzed for PCBs

Table E Sediment Concentrations of Some Organic Pollutants in the Milwaukee Harbor Estuary July 29-31, 1980. (All values are mg/kg dry weight)

Parameter	Sample Number 17a	17b	17c	18a*	18b*	18c*	18d*	
Aroclor 1248	2.9	2.1	0.60	3.0	2.7	7.8	8.5	
Total PCBs	2.9	2.1	0.60	3.0	2.7	7.8	8.5	
acenaphthene	0.45	0.78	0.32					
1,3-dichlorobenzene		0.18						
1,4-dichlorobenzene		0.79						
fluoroanthene	16.8	18.1	10.3					
naphthalene	0.40	0.95	0.47					
bis(2-ethylhexyl) phthalate	4.70	2.06	0.83					
di-n-butyl phthalate	0.16	0.14	0.10					
diethyl phthalate	0.42	0.18	0.14					
benzo(a) pyrene	5.92	6.59	3.90					
3,4-benzofluoranthene/ benzo(k) fluoranthene	13.4	13.7	7.20					
benzo(a) anthracene/ chrysene	19.5	2.05	19.4					
acenaphthylene	0.41	0.39	0.20					
anthracene/phenanthrene	6.85	9.55	7.19					
benzo(ghi) perylene	3.21	2.00	2.78					
fluorene	0.70	1.05	0.64					
dibenzo(a,h) anthracene	8.09	3.70	2.50					
ideno(1,2,3-cd) pyrene	7.64	3.66	1.75					
pyrene	8.30	11.9	8.22					

*only analyzed for PCBs.

Table E Sediment Concentrations of Some Organic Pollutants in the Milwaukee Harbor Estuary July 29-31, 1980. (All values are mg/kg dry weight)

Parameter	Sample Number							
	19a	19b	19d	21a*	21b*	21c*	21d*	
Aroclor 1254		1.9		3.6	2.9			
Aroclor 1248	2.4	3.6	0.49	6.7	7.1	3.6	0.07	
Total PCB's	2.4	5.5	0.49	10.3	10.0	3.6	0.07	
2,4-dimethylphenol	0.14							
acenaphthene	0.51	0.80	0.21					
fluoroanthene	12.5	14.3	2.65					
naphthalene	0.57	1.07	0.27					
bis(2-ethylhexyl phthalate	5.10	3.64	0.46					
di-n-butyl phthalate	0.18		0.10					
di-n-octyl phthalate	0.14							
diethyl phthalate	0.45		0.35					
benzo(a) pyrene	5.55	4.99	1.12					
3,4-benzofluoranthene/ benzo(k) fluoranthene	9.97	10.4	2.44					
benzo(a) anthracene/ chrysene	19.3	15.0	4.17					
acenaphthylene	0.36	0.70	0.14					
anthracene/phenanthrene	8.09	9.45	1.39					
benzo(ghi) perylene	4.79	3.37	0.54					
fluorene	0.78	1.24	0.25					
dibenzo(a,h) anthracene	2.59	10.2	1.33					
indeno(1,2,3-cd) pyrene	2.92	8.37	1.32					
pyrene	10.5	8.58	1.83					

*only analyzed for PCBs.

Table E Sediment Concentrations of Some Organic Pollutants in the Milwaukee Harbor Estuary July 29-31, 1980. (All values are mg/kg dry weight)

Parameter	Sample Number 22a	22b	22c	23a	23b	23c	23d	
aldrin						0.07		
4,4'-DDT					0.17	0.16	0.32	
4,4'-DDE					0.10	0.10	0.39	
4,4'-DDD					0.05	0.08	0.13	
Aroclor 1248	3.2	3.6	3.7	1.3	<0.8	<0.8	<0.8	
Total PCBs	3.2	3.6	3.7	1.3	<0.8	<0.8	<0.8	
heptachlor epoxide							0.04	
acenaphthene	2.23	1.93	3.55	11.9	1.16	2.06	2.74	
3,3'-dichlorobenzidine						0.2		
fluoroanthene	44.3	32.3	37.6	84.6	34.2	39.5	49.4	
naphthalene	0.59	0.70	1.80		0.26	0.32	0.28	
bis (2-ethylhexyl) phthalate	15.0	7.44	0.22	41.3	9.93	11.6	9.70	
butyl benzyl phthalate					1.65			
di-n-butyl phthalate	0.50		0.27	2.1	0.47	0.15	0.14	
di-n-octyl phthalate	0.32				0.30	0.26	0.33	
diethyl phthalate	1.33		1.00	8.6		0.24	0.22	
benzo(a) pyrene	15.6	9.29	15.8	35.4	9.02	12.9	17.2	
3,4-benzofluoranthene/ benzo(k) fluoranthene	26.0	22.2	24.0	40.9	21.9	21.2	29.1	
benzo(a) anthracene/ chrysene	49.8	2.87	51.0	117	31.4	48.8	64.7	
acenaphthylene	1.69	0.84	1.04		0.50	0.93	1.32	
anthracene/phenanthrene	31.6	21.5	39.9	63.9	20.5	32.2	37.6	
benzo(ghi) perylene	5.90	4.74	6.05	14.5	3.46	7.24	11.0	
fluorene	2.35	2.49	4.58	4.27	2.83	2.50	3.50	
dibenzo(a,h)anthracene	3.75	11.4	4.60	8.49	8.61	5.23	8.08	
indeno(1,2,3-cd) pyrene	6.86	9.82	5.35	14.2	8.20	6.22	9.04	
pyrene	32.8	17.0	27.4	88.0	18.9	30.4	38.8	

APPENDIX B

GUIDELINES FOR THE POLLUTIONAL CLASSIFICATION OF GREAT LAKES HARBOR SEDIMENTS

U.S. ENVIRONMENTAL PROTECTION AGENCY

REGION V

CHICAGO, ILLINOIS

APRIL, 1977

Guidelines for the evaluation of Great Lakes harbor sediments, based on bulk sediment analysis, have been developed by Region V of the U.S. Environmental Protection Agency. These guidelines, developed under the pressure of the need to make immediate decisions regarding the disposal of dredged material, have not been adequately related to the impact of the sediments on the lakes and are considered interim guidelines until more scientifically sound guidelines are developed.

The guidelines are based on the following facts and assumptions:

1. Sediments that have been severely altered by the activities of man are most likely to have adverse environmental impacts.

2. The variability of the sampling and analytical techniques is such that the assessment of any sample must be based on all factors and not on any single parameter with the exception of mercury and polychlorinated biphenyls (PCB's).

3. Due to the documented bioaccumulation of mercury and PCB's, rigid limitations are used which override all other considerations.

Sediments are classified as heavily polluted, moderately polluted, or non-polluted by evaluating each parameter measured against the scales shown below. The overall classification of the sample is based on the most predominant classification of the individual parameters. Additional factors such as elutriate test results, source of contamination, particle size distribution, benthic mecroinvertebrate populations, color, and odor are also considered. These factors are interrelated in a complex manner and their intepretation is necessarily somewhat subjective.

The following ranges used to classify sediments from Great Lakes harbors are based on compilations of data from over 100 different harbors since 1967.

	NONPOLLUTED	MODERATELY POLLUTED	HEAVILY POLLUTED
Volatile Solids (%)	<5	5 - 8	>8
COD (mg/kg dry weight)	<40,000	40,000-80,000	>80,000
TKN " " "	<1,000	1,000-2,000	>2,000
Oil and Grease (Hexane Solubles) (mg/kg dry weight)	<1,000	1,000-2,000	>2,000
Lead (mg/kg dry weight)	<40	40-60	>60
Zinc " " "	<90	90-200	>200

The following supplementary ranges used to classify sediments from Great Lakes harbors have been developed to the point where they are usable but are still subject to modification by the addition of new data. These ranges are based on 260 samples from 34 harbors sampled during 1974 and 1975.

	NONPOLLUTED	MODERATELY POLLUTED	HEAVILY POLLUTED
Ammonia (mg/kg dry weight)	<75	75-200	>200
Cyanide " " "	<0.10	0.10-0.25	>0.25
Phosphorus " " "	<420	420-650	>650
Iron " " "	<17,000	17,000-25,000	>25,000
Nickel " " "	<20	20-50	>50
Manganese " " "	<300	300-500	>500
Arsenic " " "	<3	3-8	>8
Cadmium " " "	*	*	>6
Chromium " " "	<25	25-75	>75
Barium " " "	<20	20-60	>60
Copper " " "	<25	25-50	>50

*Lower limits not established

The guidelines stated below for mercury and PCB's are based upon the best available information and are subject to revision as new information becomes available.

Methylation of mercury at levels $\geq$ 1 mg/kg has been documented (1,2). Methyl mercury is directly available for bioaccumulation in the food chain.

Elevated PCB levels in large fish have been found in all of the Great Lakes. The accumulation pathways are not well understood. However, bioaccumulation of PCB's at levels $\geq$ 10 mg/kg in fathead minnows has been documented (3).

Because of the known bioaccumulation of these toxic compounds, a rigid limitation is used. If the guideline values are exceeded, the sediments are classified as polluted and unacceptable for open lake disposal no matter what the other data indicate.

	POLLUTED
Mercury	$\geq$ 1 mg/kg dry weight
Total PCB's	$\geq$ 10 mg/kg dry weight

The pollutional classification of sediments with total PCB concentrations between 1.0 mg/kg and 10.0 mg/kg dry weight will be determined on a case-by-case basis.

a. Elutriate test results.

The elutriate test was designed to simulate the dredging and disposal process. In the test, sediment and dredging site water are mixed in the ratio of 1:4 by volume. The mixture is shaken for 30 minutes, allowed to settle for 1 hour, centrifuged, and filtered through a 0.45 u filter. The filtered water (elutriate water) is then chemically analyzed.

A sample of the dredging site water used in the elutriate test is filtered through a 0.45 u filter and chemically analyzed.

A comparison of the elutriate water with the filtered dredging site water for like constituents indicates whether a constituent was or was not released in the test.

The value of elutriate test results are limited for overall pollutional classification because they reflect only immediate release to the water column under aerobic and near neutral pH conditions. However, elutriate test results can be used to confirm releases of toxic materials and to influence decisions where bulk sediment results are marginal between two classifications. If there is release or non-release, particularly of a more toxic constituent, the elutriate test results can shift the classification toward the more polluted or the less polluted range, respectively.

b. Source of sediment contamination.

In many cases the sources of sediment contamination are readily apparent. Sediments faithfully reflect the inputs of paper mills, steel mills, sewage discharges, and heavy industry. Many sediments may have moderate or high concentrations of of TKN, COD, and volatile solids yet exhibit no evidence of man made pollution. This usually occurs when drainage from a swampy area reaches the channel or harbor, or when the project itself is located in a low lying wetland area. Pollution in these projects may be considered natural and some leeway may be given in the range values for TKN, COD, and volatile solids provided that toxic materials are not also persent.

c. Field observations.

Experience has shown that field observations are a most reliable indicator of sediment condition. Important factors are color, texture, odor, presence of detritus, and presence of oily material.

Color: A general guideline is the lighter the color the cleaner the sediment. There are exceptions to this rule when natural deposits have a darker color. These conditions are usually apparent to the sediment sampler during the survey.

Texture: A general rule is the finer the material the more polluted it is. Sands and gravels usually have low concentrations of pollutants while silts usually have higher concentrations. Silts are frequently carried from polluted upstream areas, whereas sand usually comes from lateral draft along the shore of the lake. Once again, this general rule can have exceptions and it must be applied with care.

Odor: This is the odor noted by the sampler when the sample is collected. These odors can vary widely with temperature and observer and must be used carefully. Lack of odor, a beach odor, or a fishy odor tends to denote cleaner samples.

Detritus: Detritus may cause higher values for the organic parameters COD, TKN, and volatile solids. It usually denotes pollution from natural sources. Note: The determination of the "naturalness" of a sediment depends upon the estalishment of a natural organic source and a lack of man made pollution sources with low values for metals and oil and grease. The presence of detritus is not decisive in itself.

Oily Material: This almost always comes from industry or shipping activities. Samples showing visible oil are usually highly contaminated. If chemical results are marginal, a notation of oil is grounds for declaring the sediment to be polluted.

d. Benthos.

Classical biological evaluation of benthos is not applicable to harbor or channel sediments because these areas very seldom support a well balanced population. Very high concentrations of tolerant organisms indicate organic contamination but do not necessarily preclude open lake disposal of the sediments. A moderate concentration of oligochaetes or other tolerant organisms frequently characterizes an acceptable sample. The worst case exists when there is a complete lack or very limited number of organisms. This may indicate a toxic condition.

In addition, biological results must be interpreted in light of the habitat provided in the harbor or channel. Drifting sand can be a very harsh habitat which may support only a few organisms. Silty material, on the other hand, usually provides a good habitat for sludgeworms, leeches, fingernail clams, and perhaps, amphipods. Material that is frequently disturbed by ship's propellers provides a poor habitat.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

Sediment samples were collected at 23 representative locations in the Milwaukee Estuary, Wisconsin, July 29-31, 1980. Analyses of the samples showed high concentrations of inorganic pollutants and heavy metals, and detectable levels of a number of organic priority pollutants. Contaminant concentrations are generally highest in the upper sediment layers, indicating probably recent input of pollutants to the estuary. Major source areas for various pollutants were identified. Although most industrial dischargers discharge to the Jones Island Municipal Sewage Treatment Plant via sanitary sewers, the nature and degree of sediment contamination in the estuary is comparable to major industrialized Great Lakes harbors subject to large numbers of direct industrial discharges. During rainfall events, it is possible that process wastes mixed with storm water and sewage are discharged directly to the estuary through combined sewer overflows.

17. KEY WORDS AND DOCUMENT ANALYSIS

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